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# RESEARCH MEMORANDUM

## SOME FACTORS AFFECTING FABRICATION AND HIGH-TEMPERATURE STRENGTH OF MOLYBDENUM DISILICIDE

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

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# SOME FACTORS AFFECTING FABRICATION AND HIGH-TEMPERATURE STRENGTH OF MOLYBDENUM DISILICIDE

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## SUMMARY

In an investigation of the properties of molybdenum disilicide, a fine-grain material having a moderately high oxygen content has been produced by cold-pressing and sintering, and a large-grain material having a lower oxygen content and a density of 99 percent of the theoretical density has been produced by hot-pressing.

In a series of experiments with the fine-grain material in which the only variable was the amount of carbon added, marked increases in modulus-of-rupture strength were found at carbon contents between 0.15 and 0.3 percent. Improvements in the long-time deformation properties, as shown by the flexure-creep test, and decreased high-temperature plasticity accompanied the carbon additions. The Knoop hardness was 1160.

The beneficial effects of carbon additions on strength are attributed to partial deoxidation of the material, particularly the reduction of molybdenum oxides, and the formation of silicon carbide and other carbides.

Exceptionally high short-time strengths, in comparison with other high-temperature materials, were obtained with sintered molybdenum disilicide containing from 1.0 to 1.4 percent oxygen. The effects of such oxygen contents on sintering and binding may be beneficial.

The large-grain, hot-pressed molybdenum disilicide having a low oxygen content possessed superior high-temperature deformation resistance, slightly inferior short-time strength, and decreased high-temperature plasticity as compared with the fine-grain molybdenum disilicide to which carbon was added.

## INTRODUCTION

Molybdenum disilicide ($MoSi_2$) has been found to possess several valuable properties, among them outstanding oxidation resistance and

high-temperature strength (references 1 and 2). Such a material might be of great value for use in gas-turbine engines and for other applications; a program was therefore initiated at the NACA Lewis laboratory to study factors affecting the fabrication and the preparation of $MoSi_2$ in relation to its strength at high temperatures.

The properties of extremely fine-particle-size vacuum-sintered specimens of $MoSi_2$ are compared herein with the properties of specimens investigated in reference 1. As carbon was found to have a strengthening effect on $MoSi_2$, its effect as a deoxidizing agent was investigated. Because the effect of oxygen on the strength of molybdenum disilicide is of interest, a modified hot-pressing method of preparing specimens having a comparatively low oxygen content was utilized although the method introduced changes in particle size and in other variables. In order to assure complete control of fabrication, all specimens were prepared at the Lewis laboratory.

## APPARATUS AND PROCEDURE

### Preparation of Specimens

Preparation of powders. - Two types of powder were used. Fine-particle-size powder for the carbon-addition experiments was prepared and ground as described in the appendix. For the preparation of the coarse-grain hot-pressed specimens, a commercially available high-purity -100-mesh-powder $MoSi_2$ manufactured by the Electro Metallurgical Division of the Union Carbide and Carbon Company and similar to that described in reference 2 was used.

Fine-particle powder (lot 15) for sintering and carbon-addition experiments was ground 96 hours in water. The following size determination was made by microscopic methods:

| Particle size (microns) | Percent of particles |
|---|---|
| 6 or less | 100 |
| 1 or less | 98 |

The following size determination of commercial $MoSi_2$ was made by sieve analysis:

| Mesh | Percent of particles |
|---|---|
| +100 | trace |
| -100, +200 | 24 |
| -200, +325 | 17 |
| -325 | 59 |

The commercial $MoSi_2$ for hot-pressing was ground 16 hours in cyclohexane and the following size determination was made by microscopic methods:

| Particle size (microns) | Percent of particles |
|---|---|
| Greater than 15 | 1 |
| Less than 15, greater than 11 | 1 |
| Less than 11, greater than 7 | 3 |
| Less than 7, greater than 3 | 11 |
| Less than 3, greater than 1 | 33 |
| Less than 1 | 51 |

Additions to powders. - Carbon was added to the powder in the form of powdered graphite. The constituents were blended by hand and then passed twice through a set of three 100-mesh sieves. Boron was added as molybdenum boride containing 10.03 percent boron.

Pressing. - Rectangular bars 0.2 by 0.4 by 2.5 inches were formed by pressing in a chromium-plated steel die, which was assembled in such a way as to be held together during pressing by the force of a ram acting at right angles to the pressing force (fig. 1). The die was assembled on the platen of a tensile machine and the pressing pressure was indicated on the dial. With the ram pressure released, the die could easily be disassembled and the compact readily removed.

The rectangular bars were repressed at a pressure of 40,000 pounds per square inch by the hydropress method by enclosing them in thin-walled rubber tubes that were then submerged in oil in a pressure vessel.

Sintering. - The sintering operation was carried out in a bell-jar-type vacuum induction furnace. The rectangular bars were contained in an alundum crucible wound tightly with tungsten wire and enclosed within a larger crucible. The tungsten wire, which was heated by induction, served as a highly efficient heater block and also to some extent as a radiation shield. Temperature control was manual with temperature being

determined with an optical pyrometer sighted on the specimen through a hole in the crucible cover. The indicated temperatures were held to within $\pm 20^{\circ}$ F.

In the sintering cycle, all of the specimens except the two noted in table I were

(1) Held in high vacuum in the cold furnace overnight; this was a matter of convenience although some cold out-gassing is probably advisable.

(2) Heated to a visible reddening of the specimen in 1 hour

(3) Heated to $2000^{\circ}$ F in 1 hour

(4) Held in the range $2000^{\circ}$ to $2100^{\circ}$ F for 1 hour

(5) Heat to $2500^{\circ}$ F in 1 hour

(6) Held at 2550 $\pm 50^{\circ}$ F for 2 hours

(7) Cooled in furnace with power off

Heating cycles were reproduced with no apparent variations from batch to batch. Chamber pressures were always less than 10 microns, holding at 7 microns for most of the cycle.

Hot-pressing. - Molybdenum disilicide having a low oxygen content was prepared by hot-pressing relatively coarse commercial powder (-100 mesh) containing added carbon. Pressing was done in graphite dies at a pressure of 2400 pounds per square inch; temperatures and time periods are shown in table II. The load was applied to the plunger through a 3:1 ratio lever system actuated by a hydraulic ram. Changes in volume of the compact were indicated on a scale by a pointer connected to the same lever system but reading at a 24:1 ratio. As the scale was easily read to 0.05 inch, plunger movements of 0.002 inch could be determined.

With the use of a circular plunger, flat disks 2 inches in diameter were produced. Cutting the disks with a diamond cut-off wheel produced two rectangular bars and two D-shaped end pieces per pressing.

## Evaluations

Strength evaluation. - Of the several possible methods of evaluating high-temperature strength, the modulus-of-rupture test was selected

for the short-time strength and a modification, the flexure-creep or long-time modulus-of-rupture test, was used for comparison of the long-time deformation properties.

Both short- and long-time modulus-of-rupture tests were carried out in the apparatus described in reference 1. The arrangement consisted of a specimen set on two supporting knife edges with a central opposing knife edge loaded through a lever system by a controlled flow of water into a receiver. A scale mounted behind the lever system permitted measurement of specimen deflection to 0.01 inch.

For short-time tests the water flow was controlled through a rotameter to give a rate of loading of 2000 pounds per square inch per minute. This rate of loading is that selected as standard in reference 3.

For the long-time modulus-of-rupture tests the specimens were loaded to the desired stress at the same rate and the load was maintained for the desired time. Specimens were set on a 2.0-inch knife-edge span for cold-pressed and sintered bodies and on a 1.5-inch span for hot-pressed bodies.

Chemical analysis. - Determination of molybdenum, silicon, and carbon were made by conventional means. The exact determination of molybdenum appears particularly difficult; this is born out by the compilation of Hillebrand and Lundell (reference 4). In order to obtain information concerning the precision of the molybdenum determinations on molybdenum disilicide, samples of powder were taken from a lot in such a manner as to assure uniformity; without identification, these samples were submitted to three analysts; one analyst received two samples at different times. Results were:

| Analyst | Molybdenum reported (percent) |
|---|---|
| A | 61.5 |
| B | 63.46 |
| C | 62.54 |
| C (second sample) | 63.18 |

If the results of analyst A, are disregarded, a spread of approximately 1 percent appears to be the best precision to be expected. The results are listed to two decimal places as reported by the analysts, but in the light of these analyses even the first place is not significant; therefore, limited emphasis has been placed on the analysis of the major constituents.

Oxygen determinations were made by the vacuum-fusion method at Battelle Memorial Institute. The precision of analysis was stated by the analyst to be ±10 percent of the values as given in tables I and III. Nitrogen was determined simultaneously with oxygen in a few samples. The reported value indicates the order of magnitude of the nitrogen content; as it was not intended to investigate the effect of nitrogen on the properties of molybdenum disilicide in this study, this was considered sufficient.

Silicon carbide was identified in molybdenum disilicide containing carbon as follows: 3.78 percent carbon was added to the powder and bars were pressed and sintered in the usual way. A sample was then dissolved in mixed hydrofluoric and nitric acids to leave the so-called free carbon fraction as an insoluble residue. This residue was then ignited without addition agents in an alundum boat in the conventional carbon apparatus. The material was then pulverized and powder X-ray patterns were taken. These patterns were found to coincide with those from a sample of silicon carbide.

Density determination. - Densities were determined by the water immersion method; the bars were supported during weighing on a fine wire. The weight of the wire was kept below 0.01 gram and as samples weighed approximately 20 grams, no corrections for the wire weight were necessary to obtain an accuracy of ±0.01. For pressed compacts and porous bars, the density was estimated from volumes calculated from micrometer measurements and weights.

Determination of particle size. - Microscopic methods were used for particle-size analysis. The powder sample was dispersed in acetone on a glass slide and the particles were measured with a filar eyepiece or, for the larger particle powders, photographed and measured on photographs. Measurement of particles smaller than 1 micron was not considered feasible.

Metallography. - Microscopic examination has, in general, been limited to inspection for size and distribution of voids and grain size. Early in the investigation it was discovered that because of the optical anisotropy of $MoSi_2$, polarized light brought out the grain structure of the material in a manner considered superior to and more convenient than etching (figs. 2 and 3). An etching solution of 10 grams of sodium hydroxide and 10 grams of potassium ferricyanide in 100 milliliters of water, however, was occasionally used. The solution was used at the boiling point for periods as long as 5 minutes. A sample so prepared is shown in figure 2(c).

X-ray diffraction measurements. - Standard procedures were used for obtaining powder patterns. Back-reflection patterns were taken from the surfaces of metallographic specimens at a specimen-to-film distance of 3 centimeters.

Hardness. - Knoop hardness of samples was determined using a Tukon tester with a Knoop indenter and a 1-kilogram load. Length of indentation was measured with a filar eyepiece at 500 magnification.

## RESULTS AND DISCUSSION

### Fine-Particle Sintered Material

Pressing characteristics. - Representative density relations for the material at various stages of fabrication are:

| | g/ml |
|---|---|
| Powder, bulk density | 2.0 |
| Pressed at 10,000 lb/sq in. | 3.2 |
| Repressed at 40,000 lb/sq in. | 3.7 |
| Sintered after pressing at 10,000 lb/sq in. | 6.0 |
| Sintered after pressing at 10,000 lb/sq in. and repressed at 40,000 lb/sq in. | 6.0 |

Bars of sintered $MoSi_2$ pressed at 10,000 pounds per square inch were comparatively strong and maintained sharp edges if handled with reasonable care. Bars repressed at 40,000 pounds per square inch, in addition to having higher density, were noticeably stronger in the green state, although the final sintered density was the same. Whereas the double pressing technique was used throughout the work because it produced compacts more easily handled in weighing and other operations, it appears probable that low-pressure compacting in steel dies is sufficient.

Oxygen content and densities of fine-grain bodies. - Chemical analyses of various forms of molybdenum disilicide are given in table III. The original powder (lot 15) contained 1.5 percent oxygen, which was reduced to as little as 0.15 percent by the addition of sufficient carbon. Density variations accompanying these carbon additions are shown in table I. It was apparent that although the oxygen content could be reduced, the necessity for preparing a sound body required that the amount of carbon which could be used without producing undesirable porosity be limited to 1 percent or less.

As the high-strength, cold-pressed and sintered bars contained from 1.0 to 1.4 percent oxygen and were therefore far from being pure $MoSi_2$, the density of these bars cannot very well be compared with the density of pure $MoSi_2$. Without full knowledge of the form in which

oxygen is present, the density of the mixture cannot be calculated. It was considered of interest, however, to approximate the density of $MoSi_2$ containing 1 percent oxygen. The assumptions were made that all the oxygen occurred as $SiO_2$, that the silica was in the form of $\alpha$-cristobalite (the oxide found in the surface film (reference 5)), and that it and the $MoSi_2$ would be present as a mechanical mixture. Then, for 100 grams of a 1 percent oxygen mixture, 1 gram of oxygen is equivalent to 1.88 grams of $SiO_2$ and 98.12 grams of $MoSi_2$ remain. The volume of the silica is $\frac{1.88}{2.32} = 0.81$ milliliter, and the $MoSi_2$ $\frac{98.12}{6.24} = 15.72$ milliliters. The total volume weighing 100 grams is 16.53 milliliters and has a density of 6.05 grams per milliliter or 96.9 percent of the theoretical density of pure $MoSi_2$ (6.24 grams per milliliter, reference 1). This value indicates that a marked change in density could occur in $MoSi_2$ containing oxygen. It is also probable that the sintered bars listed in table I are closer to their highest possible density than is indicated by comparison with pure $MoSi_2$.

Effects of carbon on short-time strength. - The modulus-of-rupture strength of material produced by the various methods described herein and that of the material described in reference 1 are compared at various temperatures in figure 4. The strength of some materials is not given for temperatures greater than 2000° F, as it was found that at 2200° F these bars deformed plastically to such an extent that the test had no meaning. Values at temperatures above 2000° F are given for materials which suffered only slight deformation at these temperatures; 2000° F was chosen as the general comparison temperature. Modulus-of-rupture values, densities of sintered bars, percentage of carbon added, and percentage of carbon found in the sintered bars are given in table I. As carbon additions had an effect on both density and strength, modulus-of-rupture values are given for bars of material from lot 15 in which the only variable was the density.

Marked improvements in modulus-of-rupture strength are apparent in figure 4 for all materials prepared since the preliminary investigation reported in reference 1. The strength of sintered material without carbon addition is noticeably greater than that of the material discussed in reference 1, which had a lower oxygen content and lower density. This improvement may be attributed to higher density and general improvements in technique. The addition of carbon to the sintered material also resulted in a marked improvement in short-time strength. Optimum strengths are attained when sufficient carbon is added to

leave approximately 0.15 to 0.3 percent carbon in the sintered bar (table I). As mentioned before, the amount of carbon that may be added is limited by the increase in porosity that results. A comparison of material containing 0.29 percent carbon with material to which no carbon had been added is shown on two curves of figure 4.

As these carbon additions had such a marked effect on cold-pressed and sintered material, it was considered of interest to determine the carbon and oxygen contents of the high ultimate tensile-strength, hot-pressed material reported in reference 2. The analyses were:

| Ultimate tensile strength (lb/sq in.) | Carbon (percent by weight) | Oxygen (percent by weight) | Nitrogen (percent by weight) |
|---|---|---|---|
| 42,600 at 2200° F | 0.36 | 1.4 | 0.41 |
| 37,000 at 2200° F | .22 | 2.2 | .12 |
| 42,000 at 2000° F | .20 | 2.2 | ---- |

It is evident that the high-strength forms of $MoSi_2$ contain carbon within or slightly beyond the optimum range found for the sintered specimens, and that the oxygen content, which is even higher than in the present investigation, did not detract from the outstanding strength.

A comparison of the plastic behavior of lot-15 bars with and without carbon additions is given on figure 5 in which modulus-of-rupture stress is plotted against elongation.

In addition to the deoxidizing effect of carbon, which will be discussed later, there are two other mechanisms by which carbon might affect the strength of $MoSi_2$: the formation of a new phase such as silicon carbide and the formation of an interstitial solid solution.

The method of identification previously described demonstrated that silicon carbide is formed in molybdenum disilicide containing carbon. This carbide might reasonably be expected to have a strengthening and possibly a hardening effect on $MoSi_2$.

X-ray techniques, both powder and back-reflection, showed no shifting of the lines in samples containing various amounts of carbon. In view of this lack of evidence for the formation of an interstitial solid solution, it appears possible that at least a large percentage of the residual carbon in sintered $MoSi_2$ is in the form of silicon carbide. The formation of carbides with molybdenum might also occur, especially with free molybdenum.

Effect of boron addition. - The addition of boron to $MoSi_2$ was of much less interest than the addition of carbon. Pure boron and borides are obtained with difficulty and the element is far more expensive in all forms than carbon. However, the results of a few experiments indicate that the addition of 0.12 percent boron as molybdenum boride increased the modulus-of-rupture strength of sintered bars at 2000° F from 51,000 to 88,000 pounds per square inch.

## Coarse-Grain, Hot-Pressed Material

In reference 5, it is shown that $MoSi_2$ powder oxidizes readily in air; this is probably a surface effect, reducing the particle surface area by increasing the particle size should reduce the final oxygen content. Hot-pressing appeared to be the most convenient method of fabricating high-density specimens from coarse powders. In comparing the specimens of high oxygen content with hot-pressed material, it must be noted that not only is the amount of oxygen reduced but also that, of necessity, a marked difference in particle size accompanies the change.

Forming characteristics. - Fabrication variables were investigated only enough to enable the production of high-density material. Effects of the major variables are summarized in table II, which shows that 16 hours of grinding was sufficient to produce a high density (99 percent of the theoretical) body and that a pressing temperature of 3100° F was satisfactory. Whereas the densities obtained at 3200° F are the same as for 3100° F, the strength is less. This phenomenon may be attributed to decomposition at the higher temperature. Samples made at 3100° F were therefore used for flexure-creep and other tests. The hot-pressing load was maintained for a 1/2-hour period at temperature in the hope that the time was long enough for some deoxidation to take place and yet short enough to avoid the effects of decomposition reactions. Motion of the plunger as shown by the lever system indicated that shrinkage of the compact was taking place up to the final 5 or 10 minutes of the time at temperature.

The results of chemical analyses of hot-pressed bodies are given in table III and photomicrographs are shown in figure 2. The only important impurity found in the material was iron picked up in milling. The purification process described in the appendix successfully removes iron from far finer powders but as it was desired to avoid any possibility of further oxidation and in view of the work reported in reference 2, in which no deleterious effect from similar iron contents was found, no effort was made to remove the iron contaminant.

Short-time strength. - Modulus-of-rupture values for the hot-pressed material are plotted in figure 4. The maximum strength of the hot-pressed material at a temperature of 2000° F is slightly lower than that of sintered bars. As the hot-pressed material is less plastic, strength values at 2200° F are also given. A curve showing the stress-strain relations for the hot-pressed material is presented in figure 5. Limited plastic deformation is evident as compared with the fine-particle sintered material.

## Comparison of Cold-Pressed and Sintered, and Hot-Pressed Material

Long-time properties. - A comparison of the long-time deformation as shown by the flexure-creep test for the hot-pressed material is contrasted with that for sintered bars both with and without added carbon in figure 6.

Because the flexure-creep test has not been correlated with conventional creep and stress-rupture data, the method can serve only as a comparative evaluation. The superiority of the coarse-grained, hot-pressed material having a low oxygen content is evident in figure 6, but the addition of carbon with the related reduction in oxygen content to high-oxygen-content sintered material also has a pronounced beneficial effect on long-time deformation.

Although the short-time strength of the low-oxygen-content hot-pressed $MoSi_2$ was slightly inferior to that of the fine-grain bars containing 0.29 percent carbon, the long-time deformation properties are apparently much superior. For turbine blade and other applications, the long-time properties are of the greatest importance and such a material would be superior to one having a better short-time tensile strength but poor long-time properties.

Comparison of hardness. - Representative hardness values for three forms of $MoSi_2$ are:

| Material | Oxygen (percent) | Carbon (percent) | Knoop hardness number |
|---|---|---|---|
| Hot pressed | 0.42 | 0.34 | 848 |
| Lot 15, no added carbon | 1.4 | .09 | 1065 |
| Lot 15, added carbon | 1.0 | .35 | 1163 |

Differences such as those between Knoop hardness numbers of 1163 and 1065 may not be of sufficient significance to indicate a trend. However, lower hardness for the hot-pressed material is indicated.

A Knoop hardness of 850 has been reported for hot-pressed $MoSi_2$ (reference 2) and of 1190 for siliconized wire (reference 6).

Comparison of high-temperature plastic behavior. - At elevated temperature, all materials show straight-line elastic deformation in the first part of the stress-strain curve (fig. 5). The hot-pressed material, however, exhibits a longer straight-line portion of the curve and the total deformation is much less than for the fine-particle material either with or without carbon addition.

Comparison of short-time strength. - Modulus-of-rupture strength for various representative materials now under investigation for high-temperature use are given in figure 7. It can be seen that molybdenum disilicide at 2000° F is exceeded in short-time strength only by zirconium boride.

Structure. - Photomicrographs of cold-pressed and sintered and hot-pressed $MoSi_2$ are shown in figures 2 and 3, under normal and polarized light. Differences in grain size, and shape and distribution of the voids are evident. The voids appear to be numerous and too large to correspond to the densities given, especially for the hot-pressed material at a density of 6.20. Direct observation with the microscope indicates more clearly then these photographs that a large portion of these voids have a shape and surface which may be the result of the removal of material during polishing. Improved technique in polishing can greatly reduce the number of these voids. The voids are of two types, one type is characterized by large vacanies with rough edges, and the other as small holes with conchoidal surfaces. The large voids might be explained as vacancies left behind when grains or groups of grains are torn out. The effect of overetching with the sodium hydroxide, potassium ferricyanide solution (fig. 2(c)) indicates that these pull-out holes are the first to be attacked by the etchant, an effect to be expected if the surface of the voids differs slightly in composition from the mass of the body.

The photomicrograph taken under polarized light (fig. 2(b)) shows the presence of enlarged grain boundaries for a few scattered grain faces. This phenomenon could be caused by oxide impurities at these surfaces, and it is believed that the relatively large amount of oxide present in some samples is found at these grain boundaries and results in the pull-out of material during polishing. In this connection, it may be noted that no large separate bodies of impurities have been observed in metallographic specimens of satisfactory quality, although inclusions have been found in highly impure material. Because it is believed that oxide impurities of any size would be particularly apparent under polarized light, the fine dissemination of the oxide and its possible presence in the pull-out material is indicated.

## Effect of Oxygen on Sintering and Mechanical Properties

Because of the deoxidizing effect of carbon, shown in tables I and III, it was not possible to evaluate carbon and oxygen as separate variables by the carbon addition method. The preparation of the low oxygen content, hot-pressed material introduced grain-size changes and other variables. These interrelations make it difficult to assess the effects of oxygen on such properties as strength. However, certain hypotheses may be advanced.

It has been shown (reference 5) that solid bodies of molybdenum disilicide are prevented from oxidizing by the formation of a protective coating containing silica in the form of $\alpha$-cristobalite. Also, fine-particle-size powders such as were used in the preparation of the specimens described herein were found to oxidize in air at room temperature. The oxidation of the powders would probably result in the formation of a silicious coating on the particles with the simultaneous formation of molybdenum oxides. These oxides would then be incorporated into the specimens on sintering or hot-pressing. The presence of the oxide $MoO_3$, with its high vapor pressure at 1500° F, in a sintered body might be expected to have a deleterious effect on the strength of the body at 2000° F. Part of the beneficial effect of carbon on the strength of $MoSi_2$ may be due to the reduction of traces of $MoO_3$ or other molybdenum oxides in the bodies. The strong reducing atmosphere to be expected within the graphite blocks at temperatures used in hot-pressing might also have the same effect. By this theory, a removal of only part of the oxygen could be expected to have a strengthening effect on molybdenum disilicide, a conclusion in line with the results shown in table I for the carbon addition experiments. The form in which the oxygen occurs in the body may be more important than the total quantity of oxygen but the lowest oxygen content evaluated, 0.42 percent for hot-pressed material (table III), is a quantity which might be expected to have an undesirable effect on a metal or alloy. The data of figure 7 contrasting the strength of $MoSi_2$ with that of other high-temperature materials show that if the effect of oxygen is deleterious the product still remains satisfactory by comparison.

Oxidation data (reference 5) show that the protective oxide layer on $MoSi_2$ bodies is extremely adherent. If silica in the coating adheres tightly to macroscopic bodies, it would seem possible that the powder particles might be bonded tightly together by silica in the grain boundary material. Sintering of powder compacts might be assisted by the presence of small quantities of silica. However, a silicious grain-boundary material might prevent grain growth. As the melting point of the silica (approximately 3100° F, depending on the form) is below that of $MoSi_2$ ($3500° \pm 100°$ F), the silica may be more plastic at the

sintering temperature. Although these effects of silica or other forms of the oxide appear to be either beneficial, or at least not very injurious, other effects may be deleterious and are given as possibilities. If the thermal properties of the oxide in a grain boundary were unsuitable, the thermal-shock resistance would be lowered. Plasticity in the grain-boundary material which might be beneficial to sintering might also result in increased long-time deformation. The poor deformation properties of the fine-particle-size specimens having a high oxygen content might be, at least in part, attributed to the oxygen content.

## SUMMARY OF RESULTS

In an investigation of the properties of molybdenum disilicide, a fine-grain material having a moderately high oxygen content has been produced by cold-pressing and sintering, and a large-grain material having a lower oxygen content and a density of 99 percent of the theoretical density has been produced by hot-pressing.

1. In a series of experiments with the fine-grain material in which the only variable was the amount of carbon added, marked increases in modulus-of-rupture strength were found at carbon contents between 0.15 and 0.3 percent. Improvements in the long-time deformation properties, as shown by the flexure-creep test, and decreased high-temperature plasticity accompanied the carbon additions. The Knoop hardness was 1160.

2. The beneficial effects of carbon additions on strength are attributed to partial deoxidation of the material, particularly the reduction of molybdenum oxides, and the formation of silicon carbide and other carbides.

3. Exceptionally high short-time strengths, in comparison with other high-temperature materials, were obtained with sintered molybdenum disilicide containing from 1.0 to 1.4 percent oxygen. The effects of such oxygen contents on sintering and binding may be beneficial.

4. The large-grain, hot-pressed molybdenum disilicide having a low oxygen content possessed superior high-temperature deformation resistance, slightly inferior short-time strength, and decreased high-temperature plasticity as compared with the fine-grain molybdenum disilicide to which carbon was added.

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## APPENDIX

## PREPARATION AND PURIFICATION OF MOLYBDENUM DISILICIDE POWDER

Reaction. - High-purity silicon and molybdenum as -325 mesh powder in the ratio of 2 gram atomic weights to 1 were mixed by passing them twice through a set of three 100-mesh sieves. After further hand mixing, the powders were tamped into large fire-clay crucibles and ignited with a little chromic oxide and molybdenum igniter.

Grinding. - After cooling, the semisintered mass of raw $MoSi_2$ was broken up by passing it through a jaw crusher; it was then ground in steel jar mills with the following charge: approximately 5 pounds of raw $MoSi_2$, twice this volume of steel balls graded from 1/4 to 3/4 inch in diameter, and distilled water to fill one-half the volume of the 2-gallon mills. The material was ground for 96 hours at 43 rpm.

Commercial high-purity $MoSi_2$ was ground as described except that either amyl alcohol or cyclohexane, as noted, was substituted for water in a similar charge.

Purification. - The ground material was leached with hot, 5 percent hydrochloric acid to remove iron contamination from the milling operation. The liquor was removed first by decantation and then on Buchner filters until a clean filtrate was obtained. Cold, 5 percent nitric acid was then passed slowly through the filter cake for a 3-hour period. After a water wash the cake was broken up and allowed to stand overnight in a 10 percent sodium hydroxide solution at 80° to 100° F to dissolve the silica. After filtration from the caustic solution, the material was washed with more of the hot hydrochloric acid solution for the removal of residual impurities until a clear filtrate was obtained. After a brief water wash, the cake was allowed to stand in air overnight for preliminary drying. Drying was completed in vacuum to a pressure of 1 millimeter. As $MoSi_2$ dries from a water suspension to a hard cake, it was necessary to break up the dried material in a mortar so as to pass a 100-mesh sieve. One lot of powder prepared by this method was used for all the carbon addition experiments and is referred to by its lot number, 15.

The commercial material milled in organic liquids was not purified but merely dried as much as possible on the filter and then further dried in vacuum.

## REFERENCES

1. Maxwell, W. A.: Properties of Certain Intermetallics as Related to Elevated-Temperature Applications. I - Molybdenum Disilicide. NACA RM E9G01, 1949.

2 Long, Roger A.: Fabrication and Properties of Hot-Pressed Molybdenum Disilicide. NACA RM E50F22, 1950.

3. Deutsch, George C., Repko, Andrew J., and Lidman, William G.: Elevated-Temperature Properties of Several Titanium Carbide Base Ceramals. NACA TN 1915, 1949.

4. Hillebrand, W. F., and Lundell, G. E. F.: Applied Inorganic Analysis. John Wiley & Sons, Inc., 1929, p. 880.

5. Maxwell, W. A.: Oxidation-Resistance Mechanism and Other Properties of Molybdenum Disilicide. NACA RM E52A04, 1952.

6. Beidler, E. A., Powell, C. F., Campbell, I. E., and Yntema, L. F.: The Formation of Molybdenum Disilicide Protective Coatings on Molybdenum. Jour. Electrochemical Soc., vol. 98, no. 1, Jan. 1951, pp. 21-25.

7. Lidman, W. G., and Hamjian, H. J.: Properties of a Boron Carbide-Iron Ceramal. NACA TN 2050, 1950.

8. Anon.: Metal Ceramics. Machine Design, vol. 22, no. 10, Oct. 1950, pp. 101-102.

9. Blumenthal, H., Glaser, F. W., and Steinitz, R.: Cemented Borides. Summary Report - Feb. 1, 1949 to Dec. 1, 1950. Electro Metal Corporation (Yonkers, N. Y.). (Contract N6-ONR-256, Task Order 1, NR 031-100.)

TABLE I - STRENGTH AND CARBON CONTENT RELATIONS OF SINTERED MOLYBDENUM DISILICIDE (LOT 15)

| Carbon content (percent) | | Oxygen content in sintered bar (percent) | Density (g/ml) | Modulus of rupture (lb/sq in.) | |
|---|---|---|---|---|---|
| In powder | In sintered bar | | | at 2000° F | at 1800° F |
| [a]0.08 | 0.09 | 1.4 | 6.02<br>6.02<br>5.73<br>5.73 | 50,500<br>51,000<br>[b]49,500<br>[b]51,600 | |
| .18 | .15 | --- | 5.92<br>5.92 | 87,800<br>87,200 | |
| .60 | .29 | 1.2 | 5.88<br>5.88 | 84,700<br>87,800 | 68,500<br>66,000 |
| .62 | .27 | --- | 5.82<br>5.83 | 81,800<br>84,000 | |
| .98 | .35 | 1.0 | 5.82<br>5.82 | 50,700<br>43,900 | |
| 3.78 | 1.76 | 0.15 | 4.9 | 18,300 | |

[a]Originally present in powder; no addition.

[b]Sintered for 5 min at 2550° ± 50° F.

TABLE II - EFFECT OF HOT-PRESSING VARIABLES ON DENSITY AND STRENGTH OF COMMERCIAL MOLYBDENUM DISILICIDE

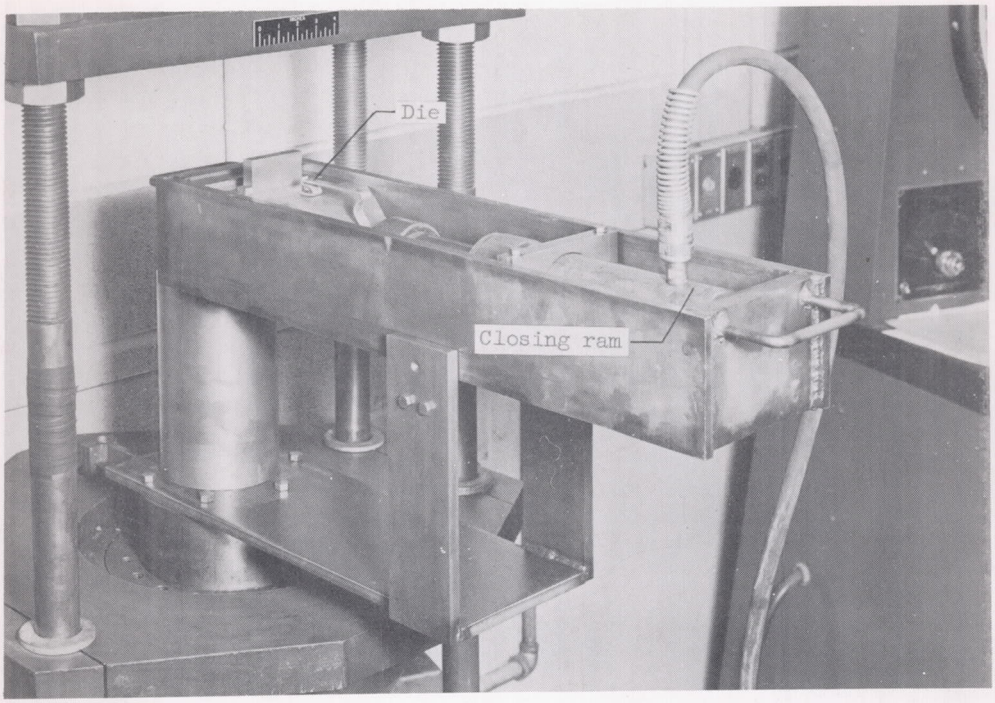
[Pressure, 2400 lb/sq in.; grinding liquid, cyclohexane.]

| Grinding time (hr) | Temperature (°F) | Time at temperature (hr) | Density (g/ml) | Average modulus of rupture at 2000° F (lb/sq in.) | Remarks |
|---|---|---|---|---|---|
| 0 | 2900 | 2 | ---- | ------ | Incipient sintering only |
| 0 | 3100 | 1/2 | ---- | ------ | Partial sintering |
| 8 | 3100 | 1/2 | 6.01 | 60,800 | |
| 16 | 3100 | 1/2 | 6.20 | 74,800 | |
| 16 | 3200 | 1/2 | 6.20 | 61,900 | |

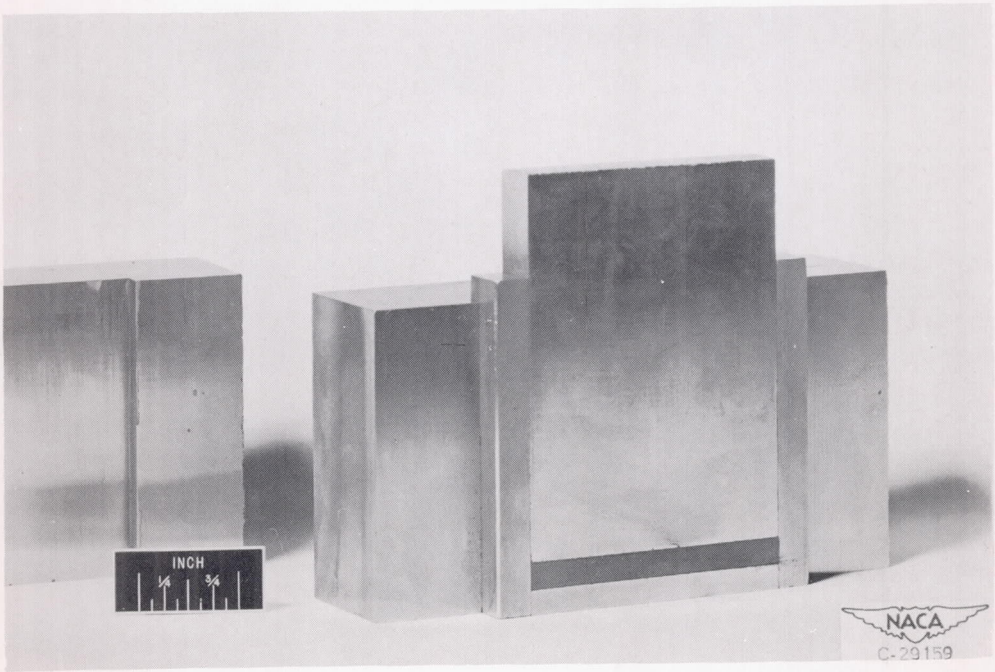
TABLE III - CHEMICAL ANALYSIS OF VARIOUS FORMS OF MOLYBDENUM DISILICIDE

| Material | Grinding Conditions | | Composition | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Grinding time (hr) | Liquid | Molybdenum (percent) | Silicon (percent) | Carbon (percent) | Oxygen (percent) | Nitrogen (percent) | Other |
| Powders prepared at Lewis laboratory | | | | | | | | |
| Lot 6, reported in reference 1 | 16 | water | 63.18 | 36.40 | 0.08 | 0.40 | 0.02 | (a) |
| Lot 15, as powder | 96 | water | 61.58 | 32.86 | .08 | 1.5 | .02 | (a) |
| Lot 15, sintered bar, no carbon addition | --- | ----- | 61.58 | 33.16 | .09 | 1.4 | ---- | (a) |
| Lot 15, sintered bar with carbon addition | --- | ----- | 62.23 | 32.70 | .29 | 1.2 | ---- | |
| Lot 15, sintered bar with carbon addition | --- | ----- | 62.72 | 33.82 | .35 | 1.0 | .04 | |
| Lot 15, sintered bar with carbon addition | --- | ----- | 63.38 | 33.56 | 1.76 | .15 | .01 | |
| Commercial $MoSi_2$ | | | | | | | | |
| As received, first lot | --- | ----- | 63.78 | 35.14 | .04 | .11 | ---- | |
| Ground | 24 | amyl alcohol | | | | .21 | .45 | 1.58 percent iron |
| Ground | 144 | amyl alcohol | 60.66 | 34.09 | .28 | 2.1 | .26 | 3.35 percent iron |
| As received, second lot | --- | ----- | 63.12 | 35.26 | .13 | .14 | .03 | |
| Ground | 16 | cyclohexane | 62.61 | 34.81 | | .35 | .02 | |
| Hot-pressed bars | --- | ----- | 62.15 | 34.79 | .34 | .42 | .03 | .82 percent iron |

[a]Spectographic analysis showed traces of iron, nickel, copper, cobalt, and chromium present.

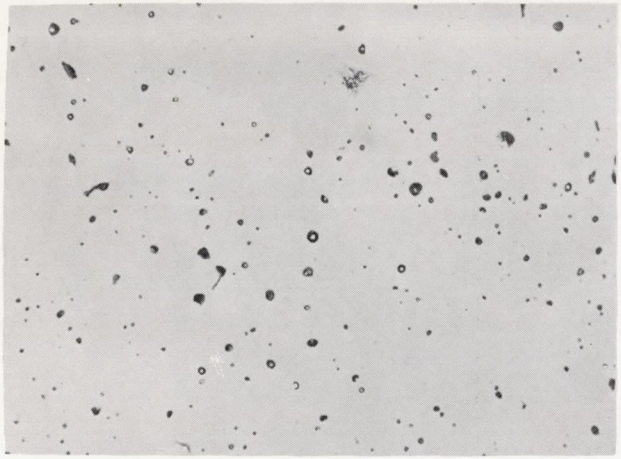



(a) Assembled for operation on platen of tensile machine.

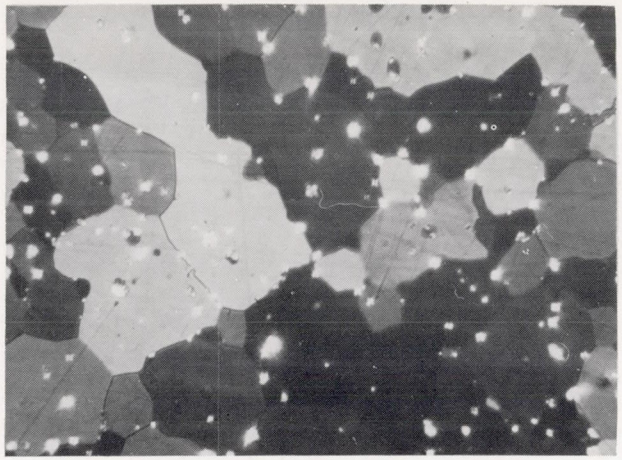



(b) Chromium-plated die opened for removal of pressed bar.

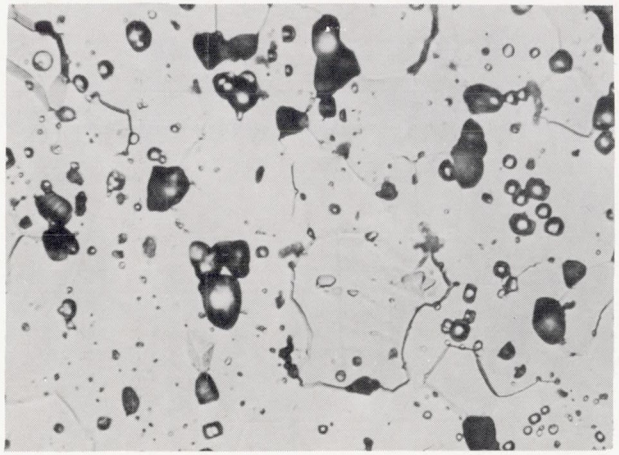
Figure 1. - Opposed pressure press used in preparation of bars.



(a) Unetched; normal light.



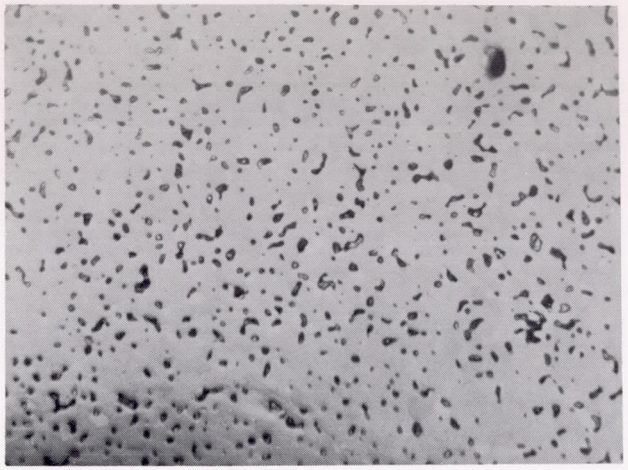
(b) Unetched; polarized light; area identical with figure 2(a).



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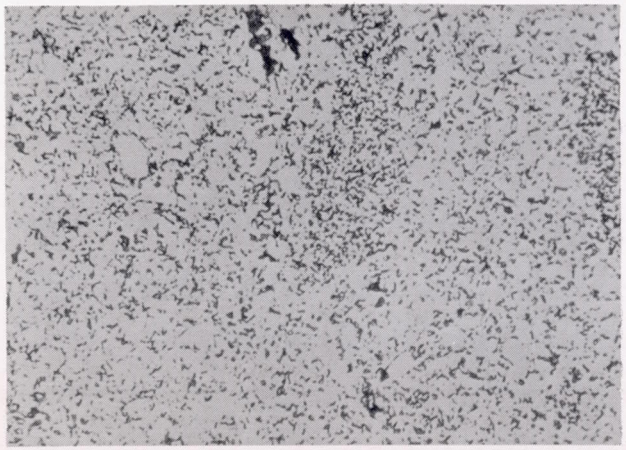
(c) Etched with potassium hydroxide and potassium ferricyanide; normal light.

Figure 2. - Photomicrographs of hot-pressed large-grain molybdenum disilicide specimen; X1000.

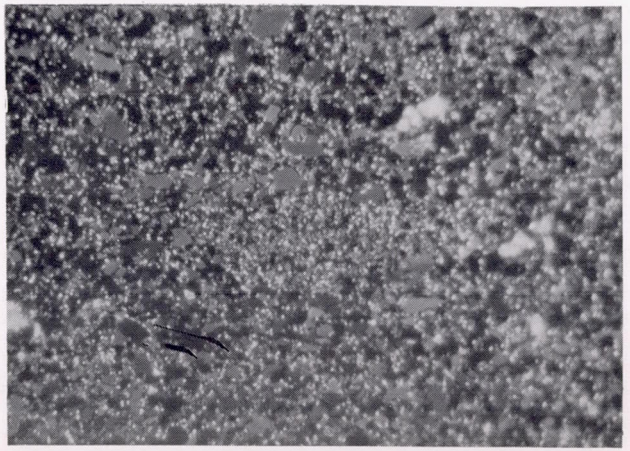


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(a) Sintered $MoSi_2$ without carbon addition; unetched; normal light.



(b) Sintered $MoSi_2$ bar containing 0.35 percent carbon; unetched; normal light.



(c) Area shown in Figure 3(b); polarized light.

Figure 3. - Photomicrographs of cold-pressed and sintered fine-grain molybdenum disilicide from lot 15; X1000.

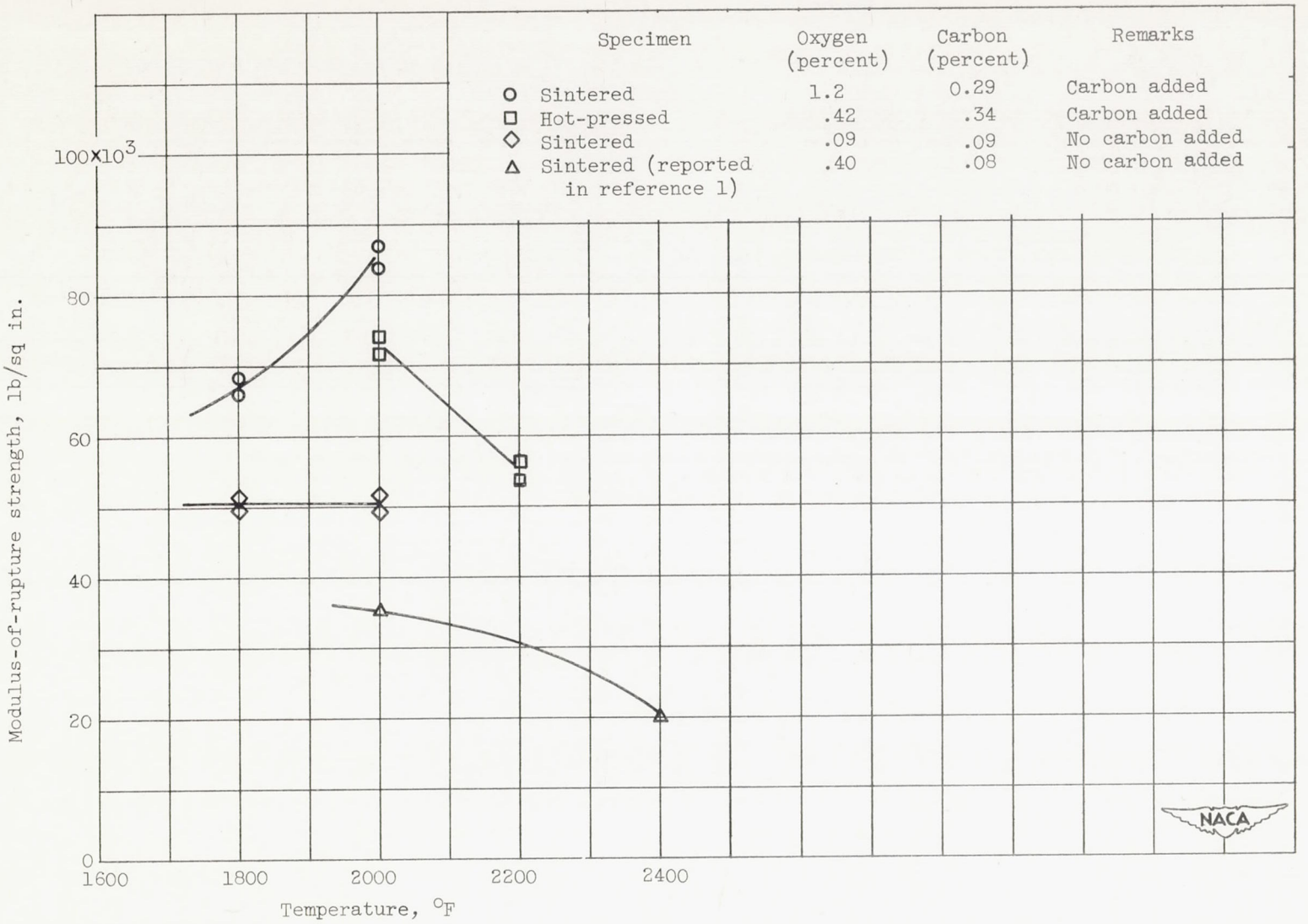



Figure 4. - Comparison of modulus-of-rupture strengths of molybdenum disilicide as produced by various methods.

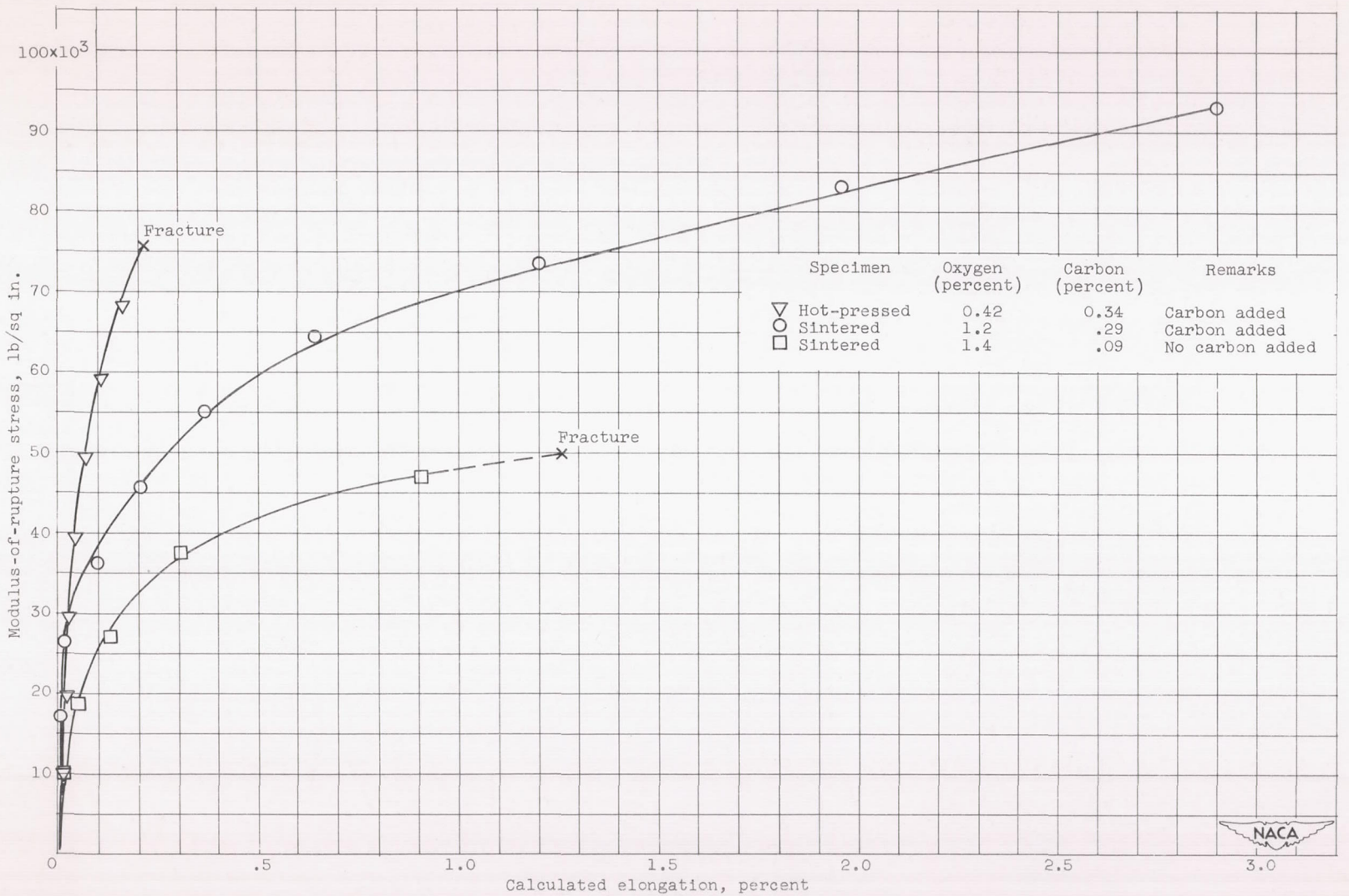
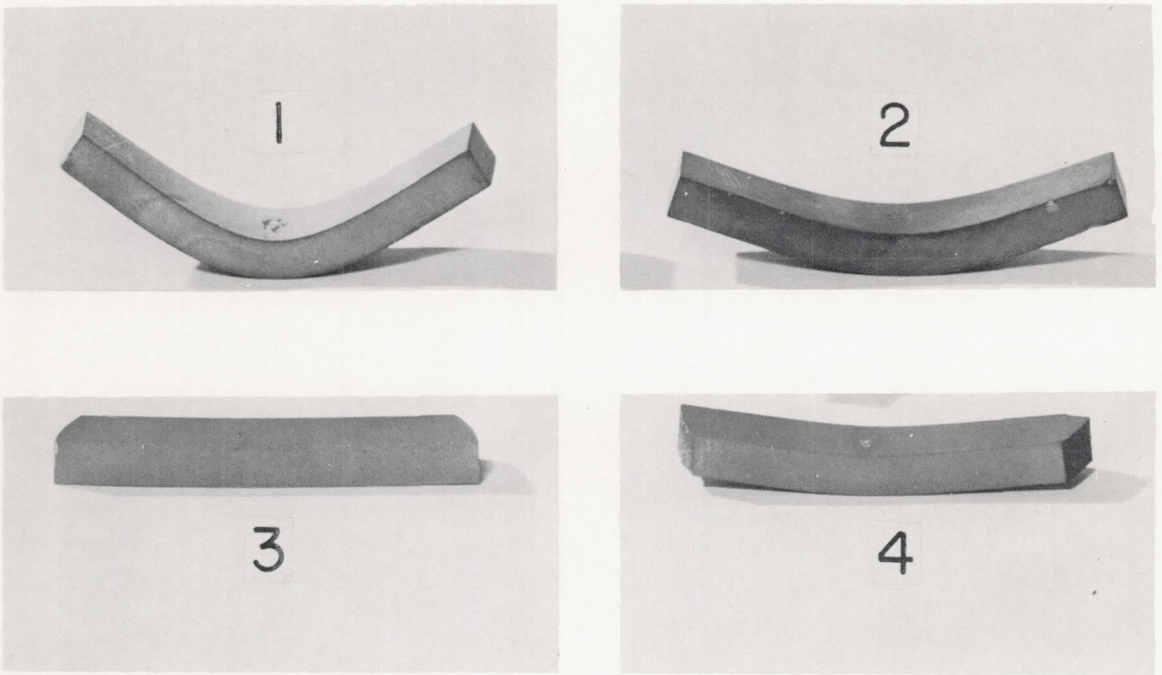



Figure 5. - Comparative high-temperature plasticity of various forms of molybdenum disilicide.




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| Specimen | Flexure stress (lb/sq in. ) | Hours under stress | Approximate elongation bottom fibre (percent) | Method of preparation | Carbon (percent) | Oxygen (percent) |
|---|---|---|---|---|---|---|
| 1 | 28,900 | $3\frac{1}{2}$ | 12.5 | Sintering | 0.09 | 1.4 |
| 2 | 28,400 | $3\frac{1}{2}$ | 2.1 | Sintering | .27 | 1.2 |
| 3 | 29,800 | 4 | - - - | Hot-pressing | .34 | .42 |
| 4 | 30,100 | 24 | 1.0 | Hot-pressing | .34 | .42 |

Figure 6. - Comparison of long-time deformation characteristics of various forms of molybdenum disilicide at 2000° F in flexure-creep evaluation.

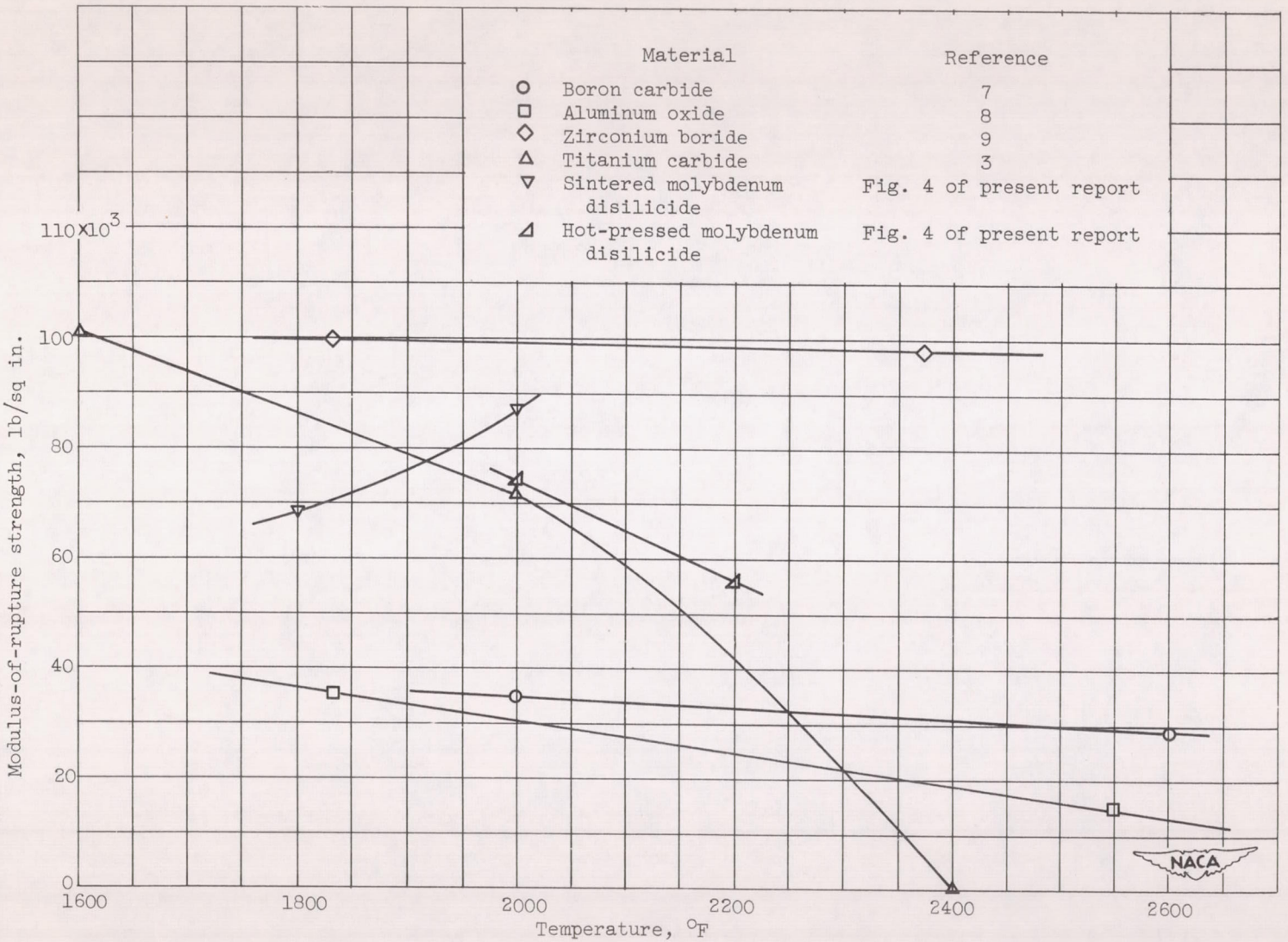



Figure 7. - Comparative modulus-of-rupture strength of five high-temperature materials.



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